

Biosorption of Chromium (VI) Using Immobilized Algal-bloom Biomass: Kinetics and Equilibrium Studies

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Abstract

The biosorption of chromium (VI) from synthetic solution using immobilized algal-bloom biomass from a wastewater treatment plant located at Bandung, West Java, Indonesia, has been studied in batch reactors. Various physicochemical parameters affected biosorption process, such as chemical activation, pH, contact time, and initial concentration of chromium (VI) were investigated. The study revealed that the highest chromium (VI) removal percentage was achieved by treating the biomass using HCl 0.1 N. The optimum removal percentage of Cr (VI) was observed at pH range of 1-3, contact time of 120 minutes, and initial Cr (VI) concentration of 100 mg/L. The biosorption equilibrium fitted well to the Langmuir Isotherm resulted in maximum adsorption capacity of 11.494 mg/g. In kinetics studies, the chromium (VI) biosorption followed pseudo-second order kinetic with k value of 0.014 g/mg min. The results indicated the potential of bloom-forming algae biomass to be used for the development of a novel, cheap, competitive, and environmentally friendly biosorbent for treating heavy metal-laden wastewater.

Keywords

Biosorption; Biosorbent; Hexavalent Chromium; Immobilized Algal-bloom Biomass; Kinetics, Equilibrium

Introduction

The presence of heavy metals in the environment at concentrations above critical values of regulatory standard is of worldwide major concern because of their nonbiodegradable and bioaccumulation characteristics, toxicity, and biomagnification in the foodchain. Chronic exposure to heavy metal ions is known to cause serious health problems such as renal dysfunction, liver damage, and some of metal ions are carcinogens and mutagens as well [(B.L. Carson, 1986), (R. Senthilkumar, K, 2010)]. Therefore, the removal and recovery of heavy metal ions from the environment is enormously important (M.A. Hashim, 2004).

Many methods have been applied in order to remove heavy metals from industrial wastewaters. Among the most commonly used procedures are chemical precipitation, ion exchange, membrane filtration, and electrochemical treatment. However, these conventional techniques are often cost prohibitive and have low efficiencies at low concentrations, particularly when metal concentration is less than 100 mg/L (G.Y. Yan, 2001). Moreover, some of these methods generate toxic sludge causing additional costs for its treatment procedures [(Z. Aksu, 2002), (Y. Zhang, 2006), (B.W. Atkinson, 1998), (H. Chen, 2005), (I. Oboh, 2009)] and need strict caution in their discharge. Therefore, it is necessary to fulfill the environmental standards at inexpensive cost. Biosorption is an emerging technology that can be easily adopted in low cost to remove heavy metals from large volume and diluted industrial wastewaters [(H. Chen, 2005), (A. Kapoor, 1995), (K. Vijayaraghavan, 2008)].

Various algal biomass exhibit different affinities and adsorption capacities towards different metals and therefore are strong candidates to be used as biosorbent materials (H. Doshi, 2007). However, the fragile structure and small size of microalgae are not suitable for continuous operations of heavy metal removal (K.H.Chu, 1997) and have led to the use of immobilized biomass. The application of immobilized biomass has several advantages including the increase of mechanical strength and resistance to chemical environment, easy separation of biomass and effluents, reducing clogging in continuous system, and repeated use in many adsorption/desorption cycles (H. Horváthová, 2009).

Cyanobacteria or blue-green algae comprises a various groups of photosynthetic bacteria that inhabit a wide range habitats (Walsby, A. E., 1994) Under

circumstances, cyanobacteria can grow excessively leading to the formation of algal blooming [(Karlson, B., 2010), (Briand, J.-F., 2003)]. To the best of our knowledge, the utilization of algal-bloom biomass naturally abundant in nature, as biosorbent, has not been widely reported. This paper presents the results of our work on biosorption of hexavalent chromium, Cr (VI), by using the immobilized bloom-forming algal biomass, including the effect of biomass activation, factors affecting the sorption process, and also kinetics and equilibrium of the process as well.

Experimental Methodology

Collection of Algal Biomass

The bloom-forming algae biomass used in this study was collected from a facultative pond of wastewater treatment plant located at Bandung, West Java, Indonesia, by using gradual filtration techniques.

Preparation of Biomass

The algal biomass collected from the pond was washed three times with tap water and subsequently rinsed with distilled water in order to remove debris and any residual solution. The biomass was then activated through chemical modification by using acid and alkaline to improve its sorptive properties. Measured amount of biomass was suspended in solutions of 0.1 N HCl, 0.1 N NaOH, and distilled water for 3 h in ratio of biomass to each solution was 1:3. The pretreated biomass was then dried in an oven for 20 h at 70°C, ground, and passed through a 50-mesh sieve (0.3 mm). The sieved powder finer than 0.3 mm was then used for the next trials.

Immobilization of Biosorbent

Immobilization of powdered biomass was carried out by using entrapment method (A. Rosevear, 1984). Measured amounts of powdered biomass was suspended in 100 mL of 2% (w/v) sodium alginate solution. The suspension of sodium alginate-biomass was then added drop wise to a stirred 500 mL of 4% CaCl₂ using a syringe. The drops of sodium alginate precipitated upon contact with CaCl₂ solution, entrapping the biomass in the form of calcium-alginate beads. These beads were then left in 4% CaCl₂ solution for 2 h to complete the hardening process and were then transferred into 0.5% CaCl₂ and stored in a refrigerator until used.

Preparation of Artificial Wastewater

Artificial wastewater containing Cr (VI) was made by weighing quantities of analytical grade potassium dichromate (K₂Cr₂O₇) and dissolved it in deionized distilled water. The solution was used as stock solution. The desired concentrations of Cr (VI) were obtained by diluting the stock solution. The pH was adjusted by using 0.1 N HCl and 0.1 N NaOH.

Measurement of Cr (VI) Ions Concentration

The concentration of Cr (VI) ions in artificial solution was analyzed by applying a colorimetric spectrophotometry method and using 1,5-diphenylcarbazide as the complexing agent (APHA, 1999). The absorbance of the solution was measured at wavelength of 540 nm.

Effect of Chemical Activation

The effect of chemical activation by using acid, alkaline, and deionized distilled water was investigated by contacting 10 g of immobilized pretreated biomass to 50 mL of 50 mg/L of Cr (VI). The mixture was then rotated on a shaker at 180 rpm for 3 h. The residual Cr (VI) in solution was analyzed spectrophotometrically.

Effect of Temperature

The effect of temperature on biosorption process was studied by contacting 10 g of immobilized biomass to 50 mL of 20 mg/L of Cr (VI) in 150 mL Erlenmeyer flasks. The flasks were then rotated on a shaker at 180 rpm for 3 h at range of temperature within 15°C-45°C. The residual Cr (VI) was measured spectrophotometrically.

Effect of Contact Time

The effect of contact time on biosorption process was investigated by contacting 10 g of immobilized biomass to 50 mL of 20 mg/L of Cr (VI). The mixtures were then rotated on a shaker at 180 rpm for 15, 30, 45, 60, 75, 90, 120, 150, 180, 210, and 240 minutes. The residual Cr (VI) was analyzed spectrophotometrically.

Effect of pH

The effect of pH solution on biosorption process was studied by contacting 10 g of immobilized biomass to 50 mL of 50 mg/L of Cr (VI). The pH solution of Cr (VI) is adjusted in the range of 1.0-6.0. The mixtures were then rotated on a shaker at 180 rpm and optimum condition of contact time and temperature. The residual Cr (VI) was measured spectrophotometrically.

Effect of Initial Cr (VI) Concentration

The effect of initial Cr (VI) concentration was studied by contacting 10 g of immobilized biomass to 50 mL of Cr (VI) solution with initial concentrations varied as 20, 50, 100, 150, 200, 250, 300, 350, and 400 mg/L. The mixtures were then rotated on a shaker at 180 rpm and optimum condition of contact time and temperature. The remain Cr (VI) was analyzed spectrophotometrically.

Equilibrium and Kinetics Studies

Equilibrium study gives the maximum capacity of adsorbates that can be adsorbed on biosorbent. It indicates the efficiency of biosorption (S.V. Gokhale, 2008). The equilibrium study in this experiment comprised two steps, i.e.: (1) studying adsorption of Cr (VI) ions on beads, and (2) fitting the data obtained into various adsorption isotherms. Optimized biosorption parameters were used for these equilibrium studies. In these experiments, beads were contacted to Cr (VI) solution of varying quantities (50-400 mg/L).

Adsorption kinetics shows the rate of adsorption that implicates to the size of effluent treatment plant. A fast kinetics of biosorption leads to short contact time and smaller treatment unit (S.V. Gokhale, 2008). Kinetics studies were conducted by contacting 10 g of beads to 50 mL Cr (VI) ion solution of varied concentrations as 50, 100, 150, 200, 250, 300, 350, and 400 mg/L. The flasks were rotated on a shaker at 180 rpm and the residual Cr (VI) ions in solution were analyzed in contact time of 5, 10, 15, 20, 25, 30, 45, 60, 75, 90, 105, 120, 150, 180, and 210 min.

Results and Discussions

Biomass Activation

Pre-treatment of biomass using NaOH and HCl resulted in an increase in Cr (VI) removal compared to distilled water (dH₂O)-washed biomass. **FIGURE 1** shows the effect of chemical pretreatment of immobilized algal biomass on Cr (VI) removal. It was observed that the percentage of metal removal obtained for both acid and alkaline-treated biomass was high in comparison with distilled water-washed biomass.

HCl-treated biomass showed the highest percentage of Cr (VI) removal (49.5%). Protonation of binding sites and removal of surface impurities after HCl-pretreatment may be the reason for the

enhancement of Cr (VI) biosorption by acid-treated biomass [(Albadarin, A. B., 2011), (Won, S. W., 2009)]. Protonated biomass favors binding metal anions (e.g. Cr (VI) ions) (Won, S. W., 2009). Hence, in subsequent trials, the experiments were carried out using acid-treated biomass. The acid-treated biomass has an advantage when applied to industrial wastewater treatment since most heavy metal polluted wastewater has acidic pH values (Y.H. Park, 1997). The NaOH-treated biomass also resulted in a slight improvement of Cr (VI) sorption may due to the crack of cells membrane that increase cells porosity.

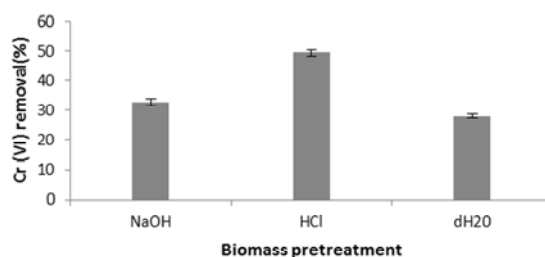


FIGURE 1 EFFECT OF CHEMICAL PRETREATMENT ON CR (VI) BIOSORPTION

Effect of Temperature

The test for observing effects of temperature on Cr (VI) biosorption by immobilized algal biomass was carried out in range of temperature between 15°C-45°C. The results are shown in **FIGURE 2**.

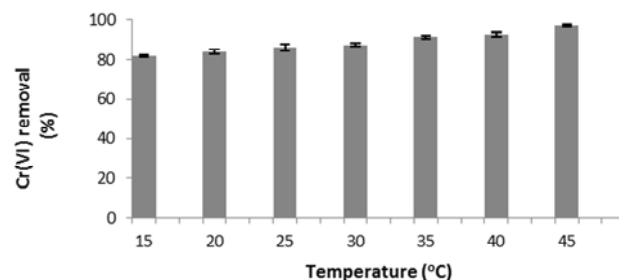


FIGURE 2 EFFECTS OF TEMPERATURE ON CR (VI) BIOSORPTION

The highest Cr (VI) removal was obtained at temperature of 45°C, while the lowest of that was found at 15°C. In general, the results showed that the higher the temperatures were, the higher the percentages of metal removal were; which indicated that the sorption processes occurred in this trial was endothermic reactions. From the results above, it was suggested that Cr (VI) adsorption by immobilized algal biomass followed energy-dependent mechanisms (N. Rangsayatorn, 2004). Similar findings were reported by Bai and Abraham (S. Bai and T. E. Abraham, 2001) on biosorption of Cr (VI) by

Rhizopus nigricans showing the increase of metal adsorption with increasing temperature.

Effect of Contact Time

The effect of contact time on Cr (VI) biosorption by algal-bloom biomass are shown in **FIGURE 3**.

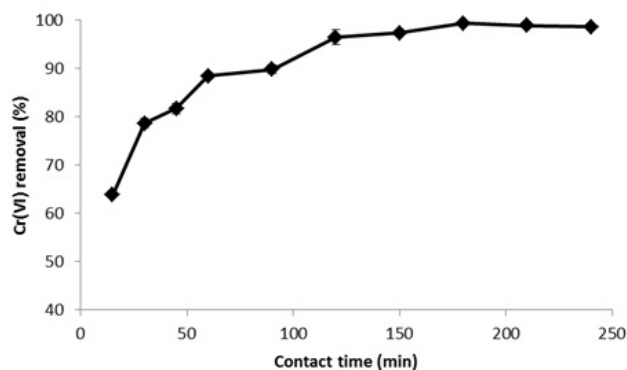


FIGURE 3 EFFECTS OF CONTACT TIME ON CR (VI) BIOSORPTION

FIGURE 3 shows that more than 50% of metal removal was achieved in the first 15 min under the tested condition. This rapid uptake of metal ions might be raised from the mixing process of suspension that overcome mass transfer resistance (M.X. Loukidou, 2004).

The highest percentage removal of Cr (VI) was observed in 180 min, the longer contact time slightly decreased metal ions sorption (**FIGURE 3**). It is indicated that at contact time longer than 180 min under this test condition, desorption rate of Cr (VI) higher than its sorption rate resulting in decrease of metal ions bound to biomass and increase of those in bulk solution. Based on the result, subsequent trials were conducted in contact time of 180 min.

Effect of pH

Previous researchers have reported that pH value is one of the main factors affecting biosorption process by various organisms [(S.V. Gokhale, 2008), (E. Hernández, 2002), (F. Pagnanelli, 2003)]. The effect of pH solution on Cr (VI) biosorption by algal biomass are given in **FIGURE 4**.

The results (**FIGURE 4**) revealed that pH values strongly influenced Cr (VI) biosorption process. The pH affects charges on the surface of biosorbent and the chemistry of metals (N. Rangsayatorn, 2004). At pH range of 1 to 3, the biomass sorbed about 20% more Cr (VI) than those at higher pH values. At low pH, the charge of overall biomass surface becomes positive, which may enhance the sorption of

negatively charged metal anions. Applying pH values >3 resulted in lower biosorption efficiency. It is in line with results reported by Rangsayatorn (N. Rangsayatorn, 2004) that the highest Cr (VI) removal by alginate immobilized *Spirulina* was achieved at pH 1.5. In accordance, it was also reported that the pH values allowing Cr (VI) sorption by microalgal biomasses were observed at highly acidic pH (≤ 2) [(E. Hernández, 2002), (M. Nourbakhsh, 1994), (S. Bai and T. E. Abraham, 2001)].

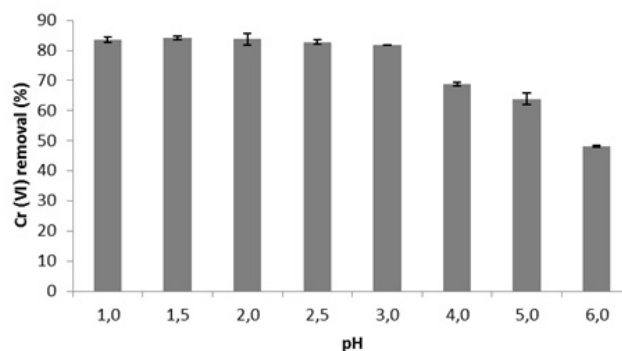


FIGURE 4 EFFECTS OF PH SOLUTION ON CR (VI) BIOSORPTION

Effect of Initial Cr (VI) Concentration

The initial metal concentration gives a driving force to overcome mass transfer resistance of metal between the aqueous and solid phase [(Z. Aksu, 2002), (Khani, 2006)]. The Cr (VI) removal efficiency was observed to be higher at lower initial Cr (VI) concentration. However, the specific metal uptake increased with increasing initial metal concentration (**FIGURE 5**).

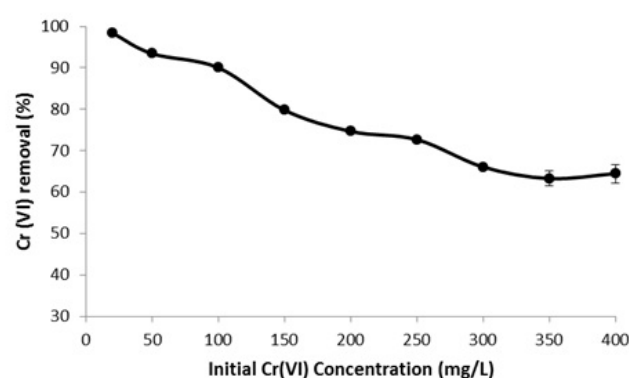


FIGURE 5 EFFECT OF INITIAL CR (VI) CONCENTRATION ON BIOSORPTION

A higher initial Cr (VI) concentration will increase the metal biosorption rate could be attributed to the higher driving force. The enhancement of metal removal with increasing of initial metal concentration could be attributed to the increase in electrostatic

interactions, involving sites with lower affinity (P.R. Puranik, 1999) and the increase in interactions between algal cells and metal ions (N. Rangsayatorn, 2004).

Kinetics and Equilibrium Studies

Kinetics and equilibrium aspects of biosorption system are important for evaluating the sorption process as a unit operation. The kinetics of sorption describing the sorbate uptake rate that controls the residence time of sorption reaction. It is related to sorption efficiency (S. Rengaraj, 2003). Moreover, information on the kinetics of metal removal is required for selecting the optimum operational conditions for up-scaling of metal biosorption process (M.X. Loukidou, 2004). Therefore, in this trial, the kinetics of chromium biosorption on algal-bloom biomass was demonstrated to understand sorption behaviour of the biosorbent and to find the biosorption rate expressions.

The rate constant of Cr (VI) biosorption was determined from the pseudo-first and second-order rate expression given by Lagergren (S. Lagergren, 1998). The differential equation for the pseudo-first rate expression is as follows:

$$\frac{dq}{dt} = k_1(qe - qt) \quad (1)$$

Integrating Eq. 1 with the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$, and rearranging the result give the following linear equation:

$$\log(qe - qt) = \log qe - \left(\frac{k_1}{2.303} \right) t \quad (2)$$

where qe and qt are amounts of adsorbed chromium (mg/g) at equilibrium and at time t (min), consecutively, and k_1 is the rate constant for adsorption (1/min).

FIGURE 6 describes the plots of $\log(qe - qt)$ versus t for one of initial Cr (VI) concentrations ($C_0 = 50$ mg/L). The values of k_1 of pseudo-first order kinetic were calculated from the slope of the linear plots (**FIGURE 6**).

The experimental data were also fitted with Ho's pseudo-second-order kinetic model (Eq. 3) (Ho, Y. S.):

$$\frac{t}{qt} = \frac{1}{(k_2 qe)^2} + \frac{1}{qe} t \quad (3)$$

The plots of qt versus t for one of initial Cr(VI)

concentrations ($C_0 = 50$ mg/L) can be seen from **FIGURE 7**. The straight line of the plots indicates the suitability of the above equation (Eq. 3).

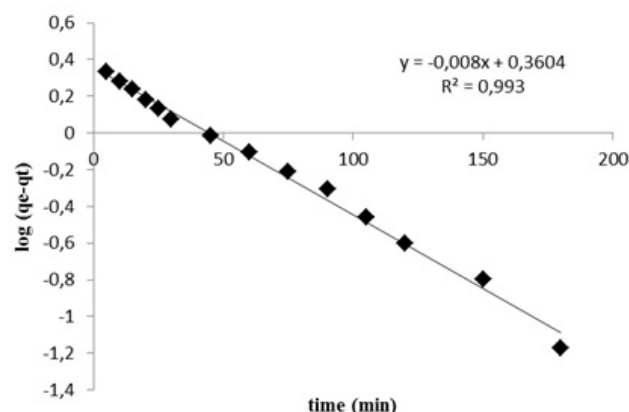


FIGURE 6 LAGERGREN PLOTS FOR THE PSEUDO-FIRST ORDER KINETIC OF CR (VI) BIOSORPTION ON ALGAL BIOMASS

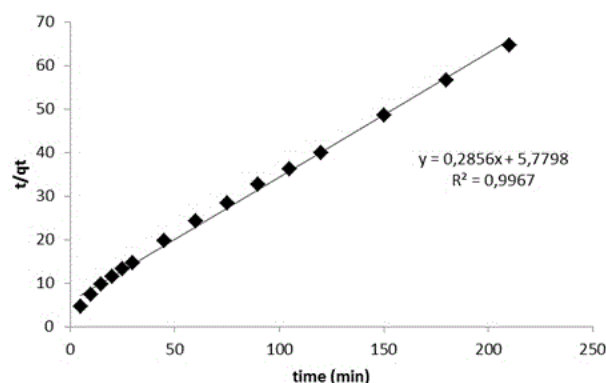


FIGURE 7 PLOTS FOR THE PSEUDO-SECOND ORDER KINETICS OF CR(VI) BIOSORPTION ON IMMOBILIZED ALGAL BIOMASS

The experimental data best fitted with Ho's rate expressions for the pseudo-second order kinetics (**TABLE 1**). It can be seen from the correlation regression coefficients, R^2 , of the pseudo-second order kinetic, which is slightly higher than that of the pseudo-first order. Hence, it might be concluded that Cr (VI) biosorption kinetics under this trial condition followed the pseudo-second order kinetic.

Trials were also performed at an attempt to understand the equilibrium process of Cr (VI) biosorption on the algal biomass. The obtained data were fitted with numerous adsorption isotherms, namely the linear, Langmuir, and Freundlich isotherms. These isotherms relate metal uptake per unit weight of adsorbent S to the equilibrium adsorbate concentration in the bulk fluid C_e . The linear model describes the accumulation of solute by adsorbent as directly proportional to the solution

concentration:

TABLE 1 SORPTION RATE EXPRESSION FOR DIFFERENT INITIAL CR (VI) CONCENTRATIONS

Initial Concentration of Cr (VI) (mg/L)	Rate Constant		R ²	
	Lagergren Pseudo-first Order, k_1 (1/min)	Ho Pseudo-second Order, k_2 (g/mg min)	Pseudo-first Order	Pseudo-second Order
50	0.018	0.014	0.993	0.996
100	0.016	0.009	0.991	0.995
150	0.014	0.006	0.994	0.891
200	0.014	0.008	0.982	0.997
250	0.014	0.004	0.995	0.994
300	0.014	0.003	0.996	0.994
350	0.014	0.003	0.900	0.993
400	0.014	0.003	0.984	0.995

$$S = k_d C_e \quad (4)$$

The distribution coefficient, k_d is often referred as the partition coefficient.

The Langmuir model assumes uniform energies of adsorption onto the surface and has been widely applied to systems that exhibit maximum adsorption capacities. The Langmuir isotherm is given by:

$$S = \frac{q_m k_{ads} C_e}{(1 + k_{ads} C_e)} \quad (5)$$

where S and k_{ads} are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. It is usually linearised to obtain the following form:

$$\frac{1}{S} = \frac{1}{q_m} + \frac{1}{q_m k_{ads}} C_e \quad (6)$$

The Freundlich isotherm is the most widely used non-linear sorption model:

$$S = k_f C_e^{1/n} \quad (7)$$

where k_f relates to sorption capacity and $1/n$ to sorption intensity. The logarithmic form of Eq. 7 is

usually applied to fit data from equilibrium study as follows:

$$\log S = \log k_f + \frac{1}{n} \log C_e \quad (8)$$

FIGURE 8, 9, and 10 describe the linear, Langmuir, and Freundlich isotherm plot for Cr (VI) biosorption onto immobilized algal biomass. These plots were used to calculate the isotherm parameters shown in TABLE 2.

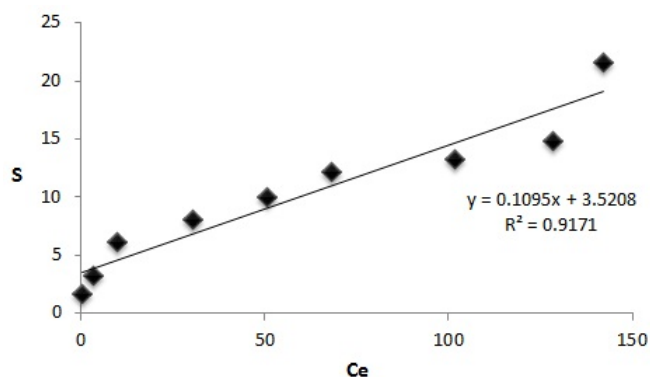


FIGURE 8 THE LINEAR ISOTHERM PLOT FOR CR(VI) BIOSORPTION ON IMMOBILIZED ALGAL BIOMASS

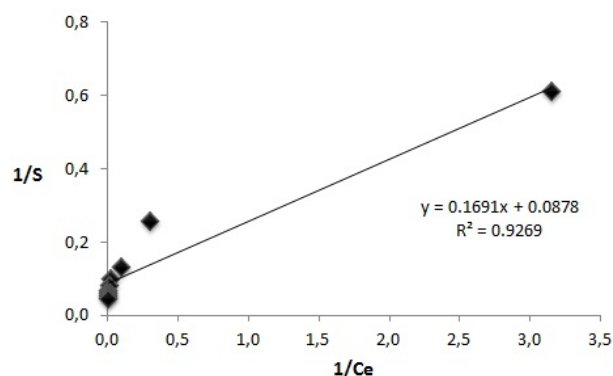


FIGURE 9 THE LANGMUIR ISOTHERM PLOT FOR CR(VI) BIOSORPTION ON IMMOBILIZED ALGAL BIOMASS

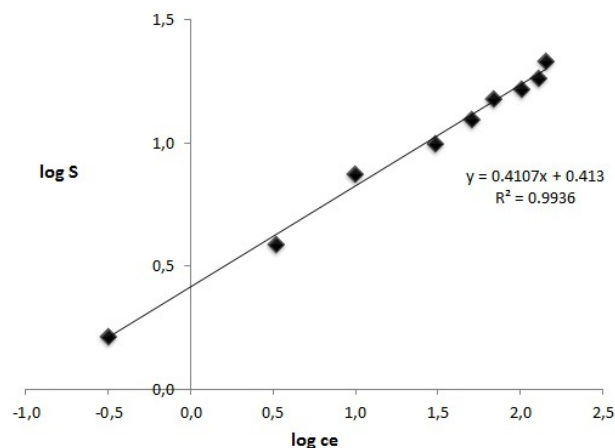


FIGURE 10 THE FREUNDLICH ISOTHERM PLOT FOR CR(VI)

BIOSORPTION ON IMMOBILIZED ALGAL BIOMASS

As can be seen from **FIGURE 8, 9, 10**, the equilibrium Cr(VI) biosorption by immobilized algal biomass followed the Linear, Langmuir, and Freundlich isotherms. The values of adsorption capacity (k) and intensity of adsorption (n) are given in **TABLE 2**.

TABLE 2 SUMMARY OF ISOTHERM PARAMETERS

Parameter	Linear Isotherm	Langmuir Isotherm	Freundlich Isotherm
R^2	0.917	0.926	0.993
$1/n$	-	-	0.410
k_f	-	-	2.588
qm (mg/g)	-	11.494	-
k_{ads}	-	0.515	-
R_L	-	0.005-0.088	-
k_d	0.109	-	-

A dimensionless separation factor of the Langmuir isotherm, R_L , indicates the favorability characteristic of sorption process, i.e., favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$). The R_L value of sorption system obtained from this study was found to be between 0.005 and 0.008, showing a favorable adsorption process.

The correlation regression coefficient, R^2 , of Linear isotherm closes to 1, but the k_d value much lower than 1. It indicates that the Linear isotherm can not describe the Cr (VI) biosorption very well. Based on the results, it might be concluded that Cr (VI) biosorption on immobilized algal biomass best fitted with Freundlich isotherm with $1/n$ 0.410 and R^2 0.993. Beside that, the biosorption also described well by the Langmuir isotherm with qm is obtained of 11.494 mg/g and R^2 of 0.926.

Conclusion

The immobilized algal biomass has been characterized as a potential biomaterial for removing heavy metal ions from heavy metals-containing wastewater. The Cr (VI) biosorption was characterized as a temperature-dependent reaction at a range of temperature from 15°C to 45°C, which the best metal removal that maintained biosorbent integrity was found at 35°C. In addition, it has been identified that

pH solution, initial metal concentration, and contact time affected biosorption process by immobilized algal-bloom biomass. The kinetics data revealed that the biosorption process followed the second-order kinetic, indicating the rapid process of metal removal by immobilized algal-bloom biomass. The equilibrium data fitted well with Freundlich and Langmuir isotherm and resulted in maximum metal uptake of 11.494 mg/g. In general, we concluded that the immobilized bloom-forming algae biomass could be exploited further as a cheap, eco-friendly, and competitive biosorbent for treating heavy metals-containing wastewater.

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